



Short communication

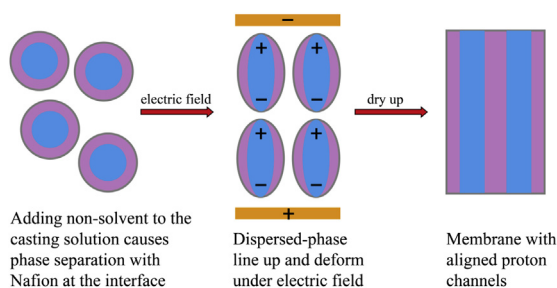
Electro-casting of proton exchange membranes from a heterogeneous solution

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HIGHLIGHTS

- Non-solvent CCl₄ leads to phase separation of the casting solution of Nafion.
- Electric field treatment to the solution leads to improved proton conductivity.
- Proton channels of the PEM are oriented in the trans-plane direction.
- The PEMs are mechanically robust despite of phase separation in casting solution.
- It is suggested that the non-solvent induced phase separation is a deciding factor.

GRAPHICAL ABSTRACT



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ABSTRACT

A novel solution casting method of membrane preparation is explored to improve the conductivity of proton exchange membranes (PEMs). A high voltage alternative electric field is applied to a heterogeneous Nafion solution while evaporating the solvents, leaving aligned proton channels in the solidified membrane, and SAXS and WAXS have been given as direct evidences. Therefore, the trans-plane conductivity of the PEM is increased. A Non-solvent of low polarity carbon tetrachloride (CCl₄) causes phase separation in the casting solution, which facilitates the Nafion ionomer to respond to the applied electric field. Despite the severe phase separation in the casting solution, the resultant electro-casting membrane shows a higher mechanical strength than that of the normal recast Nafion membrane.

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1. Introduction

Polymer electrolyte membrane (PEM) fuel cells are considered to be a very promising alternative power source for a wide

spectrum of applications. The PEM in such fuel cells is often a performance-limiting component. Perfluorosulfonic acid membranes with the trade name Nafion are the most commonly used electrolyte in PEM fuel cells. Although the Nafion has become the PEM of choice since the late-1960's and is still among the best available, it is not satisfactory in conductance property, which can lead to problems, such as ohmic losses at high current density, resistance to water transport from cathode to anode, or proton

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conductance deterioration at high temperature or low humidity [1]. Therefore, numerous efforts have been made to improve the conductivity performance of Nafion membranes. Generally, the increase in ion exchange capacity (IEC) of PEMs can significantly elevate the conductivity, however, high IEC is usually achieved at the sacrifices of other properties of the PEMs, such as the mechanical stability and solvent resistance [2].

One attractive approach of improving the conductivity of PEMs is to construct straight proton conducting channels, since under such condition the utilization of sulfonate groups can be improved, and therefore high conductivity can still be expected even with a relatively low IEC. To this end, electric field treatment has been suggested as a method for achieving oriented proton channels in PEMs [3]. Molecular-dynamics simulations have been used to study the morphological changes induced in ionomer by imposition of a strong electric field, and it has been observed that upon removal of the electric field, the structures aligned along the direction of the applied field persist and have a lower calculated free energy than the original isotropic morphology [4].

Some researchers have used the electric field to construct oriented proton channels in PEMs. Three orders of magnitude enhancement of conductivity was obtained by Gasa et al. [5] and Wei and Yate [6] who have applied an electric field to hybrid polymers that blend non-conductive matrix polymers with conductive sulfonated poly (ether ketone ketone) or Nafion solid particles. However, the conductive component is the dispersed phase with low volume fractions slightly lower than the percolation threshold. This can cause great improvement in conductivity after the electric field is applied, but the value of the conductivity remains relatively low even after being improved. What is more, by dispersing a conductive component into a non-conductive matrix, the conductivity of the hybrid membranes is limited, which can never be higher than that of the conductive component by itself. On the other hand, the electric field treatment will be less effective given the conductive phase is the major component of PEMs. Therefore, a hybrid PEM containing a minority conductive dispersed phase is not a good system where to construct oriented proton channels.

In this communication, a method of electric field treatment has been established to synthesize a PEM with oriented proton channels using only Nafion as the ionomer. Besides the Nafion ionomer and solvent DMF, the casting solution also contains a low polarity non-solvent CCl_4 which induces intense phase separation in the casting solution. Conductivity and mechanical strength of the PEM have been measured. Crystallinity of the PEM is obtained from the X-ray diffraction (XRD) spectrum.

2. Experiment

2.1. Membrane preparation

Commercial Nafion solution (5 wt %, DE520) was purchased from Aldrich. The received Nafion solution was heated in a vacuum oven at 333 K to obtain dry Nafion resin, which was then redissolved in DMF to get a 10 wt % solution. CCl_4 was mixed with the solution under agitation to obtain an opaque 3.8 wt % Nafion casting solution. A membrane was obtained by casting the opaque solution under an alternative electric field (4500 V cm^{-1} , 0.1 Hz) on a glass plate at 353 K for 12 h, and then at 373 K for 4 h. The membrane prepared using the described method is denoted as M1 and another membrane prepared following exactly the same procedure but without applying the electric field is denoted as M2. A conventional recast Nafion membrane obtained from a 10 wt % Nafion/DMF solution was also prepared under identical conditions, which will be referred to as M3. The membranes were peeled off from the glass plates in deionized water, then protonated by

immersing in 1 mol dm^{-3} sulfuric acid solution at room temperature for 24 h and rinsed thoroughly with deionized water. The thickness of the membranes in dry state is approximately 70 μm .

2.2. Characterization

The proton conductivities in the in-plane and trans-plane directions of the PEMs are measured following the method described in our previous works [7,8].

The small-angle X-ray scattering (SAXS) and wide-angle X-ray scattering (WAXS) measurements were conducted using an X-ray diffractometer (Rigaku D/Max-2500V-PC, Rigaku) with a $\text{Cu K}\alpha$ source ($\lambda = 1.54 \text{ \AA}$) at 40 kV, 200 mA. The samples of membrane were immersed in deionized water for a week before testing to ensure full hydration. The same instrument was also used to obtain XRD data, from which the crystallinity of membrane was obtained by first identifying the crystalline (at $2\theta = 14.5^\circ$) and amorphous (at $2\theta = 16.5^\circ$ and 39.7°) peaks, and then calculating the ratio of the crystalline peak area to the sum of the three peak areas [9].

A sealed cell of the heterogeneous solution was put under an alternative electric field (4500 V cm^{-1} , 0.1 Hz) of trans-plane direction at room temperature without evaporation. The resistance of the solution in the in-plane direction varied with time, which was monitored by a frequency response analyzer (FRA, PARSTAT® 2273, Princeton Applied Research Inc.).

The composition of the dispersed phase and continuous phase in the heterogeneous solution is separately analyzed by a gas chromatograph-mass spectrometer (GC-MS, QP5000, Shimadzu Co.). Samples taken from casting solutions were diluted with an appropriate amount of DMSO and injected directly into the GC.

The mechanical strength of the membranes is measured using an electronic universal testing machine (WD-10D, Changchun Second Tester Factory). The sample preparation and measurement procedures are carried out in accordance with the Chinese Standard GB-13022-91.

3. Results and discussion

3.1. Conductivity

M1 has priority over M2 in the trans-plane conductivity from 293 to 333 K (Fig. 1a). However, the conductivities in orthogonal directions should be inversely proportional for PEMs with oriented proton channels, which has been observed by Majewski et al. [10]. To further certify the orientation of proton channels in the M1, in-plane conductivity of the PEMs has been measured and shown in Fig. 1b that the M2 takes priority over the M1 in the in-plane conductivity from 293 to 353 K. Such phenomena of inverse proportion indicate that the proton channels in the M1 sample have been oriented in the trans-plane direction by the electric field. Compared with random proton channels, the oriented proton channels can shorten the proton transport distance through PEMs and improve the utilization of the sulfonate groups in ionomer. As a result, the resistance of PEMs can be decreased with a constant thickness and IEC of the PEMs, and high mechanical strength and solvent resistance could be expected.

In addition, the higher conductivity of M1 and M2 over that of M3 implies that without the electric field treatment the non-solvent by itself can also contribute to the conductivity improvement, which makes another story [11].

3.2. Crystallinity and mechanical analysis

As properties of the PEMs are strongly affected by their micro-phase separated morphology, works have been done with the aim

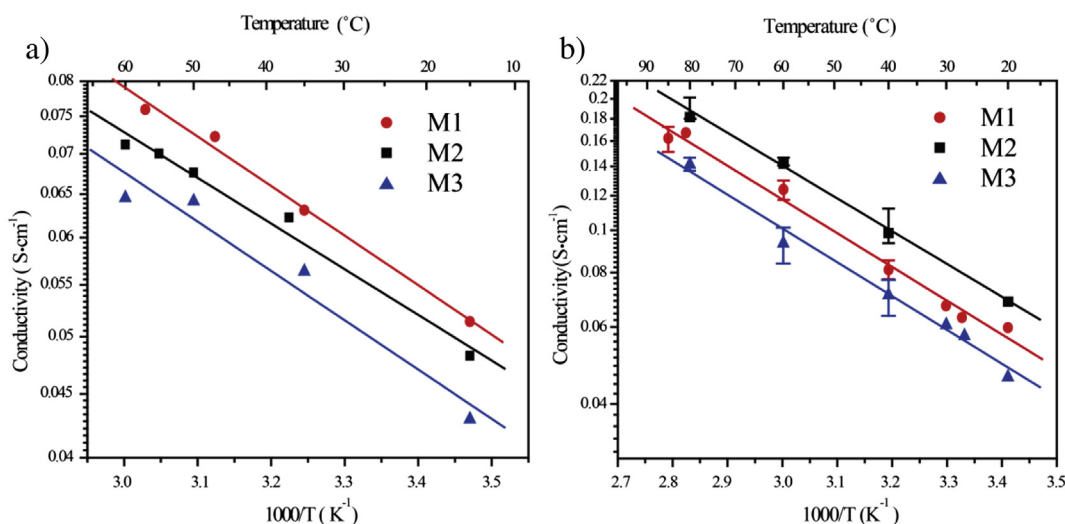


Fig. 1. Conductivity of the PEMs in different directions (a) trans-plane and (b) in-plane direction under saturated humidity.

of microphase morphology control. Zhang et al. [12] added to the casting solution a “molecular gelator”, dimethylbenzaldehyde, and induced crystallinity increase and mechanical strength enhancement. The non-solvent CCl_4 and external electric field have also caused morphology change in the PEM. As shown in Table 1, the crystallinity of M2 is lower than that of M3, suggesting that ionomer chains in the M2 are not able to pack closely because of the phase separation in casting solution caused by the addition of CCl_4 . However, casting the same heterogeneous solution under an electric field, a crystallinity increase in the M1 by around 51% of that in the M2 is achieved, which suggests that the electric field induced dipolar attraction has packed the carbon–fluorine chains of M1 in a tight and ordered pattern. Moreover, possessing a Stress at break of 11.8 MPa, the M1 is a robust membrane. But such high stress is inconsistent with the common experience that casting from poor solvents would always result in fragile membranes. Casting from such a heterogeneous solution, a membrane of low stress would normally be expected. Presumably the electric field induced ionomer self-organization has packed the ionomer chains tightly and makes the M1 exceptional.

3.3. SAXS and WAXS

SAXS and WAXS have been measured, and the spectrums are given in Fig. 2 as a direct evidence of orientation of the proton channels in the PEM. With electron density differences between the ionic domains and the PTFE matrix, a scattering maximum appears in WAXS profiles at $q = 1\text{--}2\text{ nm}^{-1}$, which has been termed the “ionomer peak”. In addition, a very low angle peak or shoulder in SAXS is often observed around $q = 0.5\text{ nm}^{-1}$, which has been attributed to scattering from the locally ordered crystallites composed of relatively long runs of PTFE segments between side chains [13,14]. The peak of M1 at around 1.4 nm^{-1} in the WAXS spectrum represents oriented clusters of hydrated sulfonate

groups, whereas the spectrums of M2 and M3 show no scattering maximum. The higher SAXS intensity of M1 proves that the electric field assisted packing of the Nafion molecules gives the PTFE segments an ordered pattern, which in turn results in a higher crystallinity (Table 1).

3.4. Response of the heterogeneous solution to the electric field

Resistances of the heterogeneous solution changing versus time under an electric field are shown in Fig. 3. The resistances measured in the in-plane direction will be higher if more conductive groups are aligned in the trans-plane direction by the electric field.

The resistance of Nafion/DMF solution does not change in response to the electric field in the absence of CCl_4 , which implies that the conductivity of PEMs electro-casting from a homogeneous solution cannot be affected by the electric field. With the CCl_4 content increasing, significant electric field response of the resistance is determined at the CCl_4 content of 46.6%, overlapping with the concentration where phase separation happens (the solution becomes opaque). This concentration overlapping confirms that the orientation of proton channels under the electric field arises from the interactions between the electric field and the dispersed phase in the heterogeneous solution.

The time cost for a significant resistance increase under the electric field is instructive. Taking the solution of 56.6% CCl_4 content as an example, it takes 10 min for the solution resistance to acquire a significant increase without any solvent evaporation. This information is useful in choosing boiling point of the non-solvent to make the phase-separated morphology persist long enough for the electric field to become effective during solvent evaporation.

Compositions of the two phases in the heterogeneous solution have been measured separately. Though the heterogeneous solution can stay stable for at least four weeks, it is separated into two layers by gravity settling for three months. The supernatant and infranatant originate from the continuous phase (CCl_4 /DMF liquid) and the dispersed phase (Nafion solid and CCl_4 /DMF liquid) of the heterogeneous solution, respectively. Revealed by GC–MS, the mass ratio of CCl_4 /DMF in the supernatant and infranatant layer is 1.65 and 1.34, respectively, while in the heterogeneous solution mixture the ratio is 1.51. The relatively low CCl_4 content in the infranatant layer represents a hydrophilic dispersed phase, whereas the continuous phase (supernatant) acquired more CCl_4 which makes it more hydrophobic. The Nafion molecules which consist of a

Table 1
Mechanical strength of the PEMs and crystallinity data calculated from integration of the XRD spectrums.

	M1	M2	M3
Crystallinity (%)	27.2	18.0	21.3
Stress at break (MPa)	11.8	8.3	9.2

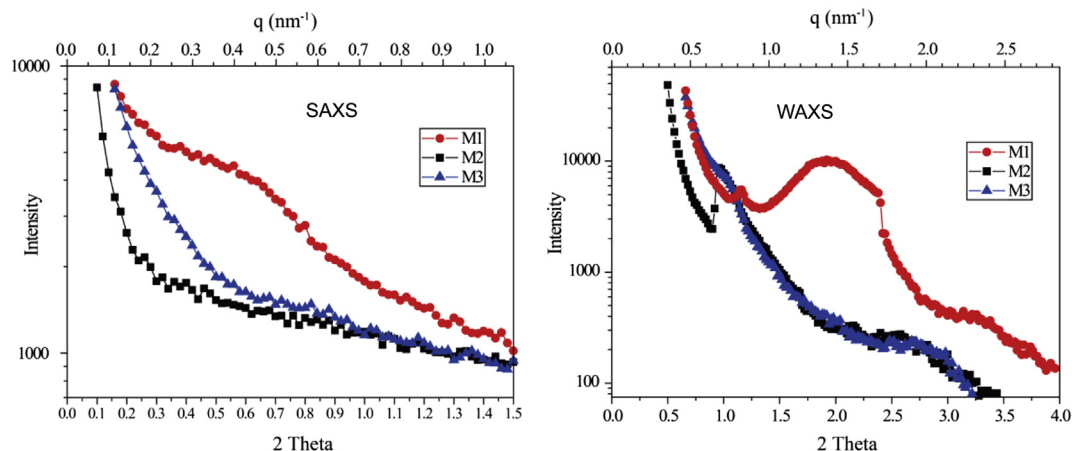


Fig. 2. SAXS and WAXS spectrums of Nafion membranes cast from different procedures.

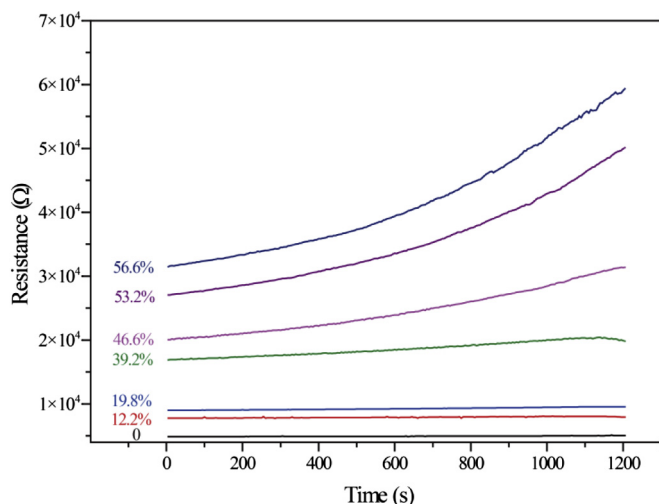


Fig. 3. Resistance of the heterogeneous solution in the in-plane direction at various CCl_4 contents under an electric field of trans-plane direction at room temperature.

hydrophobic part and a hydrophilic part are supposed to be at the interface of the two phases serving as a surfactant stabilizing the phase-separated solution. According to the typical surfactant behavior in biphasic mixtures, the hydrophilic “head” of Nafion is supposed to insert into the hydrophobic dispersed phase with the hydrophobic “tail” vibrating in the hydrophobic continuous phase (Fig. 4). The stableness of such heterogeneous solution also supports this “surfactant and phase separation model”.

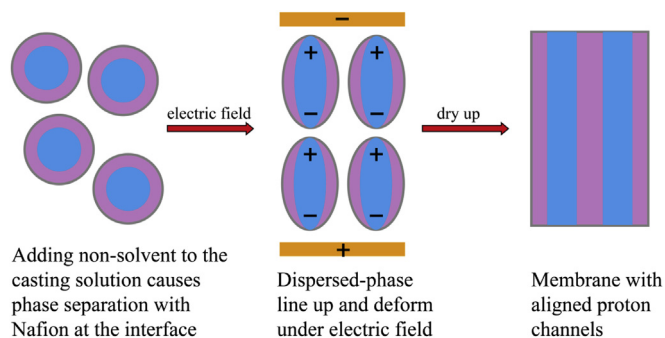


Fig. 4. Scheme of the electric field induced orientation in a heterogeneous solution.

Based on the model, the mechanism of electric field induced orientation of proton channels is suggested. The electric field induces a polar attraction force between the dispersed phase droplets which align and deform into a straight line, and the Nafion molecules which spread at the interface of the two phases are oriented simultaneously.

4. Conclusion

A Nafion membrane with oriented proton channels is prepared using a novel electro-casting method with the involvement of a non-solvent CCl_4 . The heterogeneous solution shows a sensitive response to an external electric field and results in a proton exchange membrane with oriented proton channels in the trans-plane direction, therefore, the trans-plane conductivity of the membrane is increased. Though the increase in the trans-plane conductivity of the PEM after the electric field alignment is 10% to the most, further evidence for the orientation of sulfonate clusters is given by SAXS and WAXS. The in-plane resistance of casting solution in response to the application of a trans-plane electric field also indicates the possibility of aligning the proton conductive channels in the direction of the electric field. The membrane is mechanically robust, despite of severe phase separation in the casting solution. Based on the compositions of the two phases in the heterogeneous solution, the mechanism of the external electric field induced orientation of proton channels has been suggested that the enhanced performance of the membrane results from the interactions between the electric field and the dispersed phase in the casting solution.

Acknowledgments

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